Indian J. Phys. **54B**, 357-365 (1980)

Laser induced spectroscopy of diatomic molecules

D K Rai

Department of Physics

Banaras Hindu University, Varanasi-221005, UP

Analysis of the spectrum of diatomic molecules at the highest available level of resolution and dispersion is a proven method of elucidating important aspects of their electronic structure. Keeping in view the long history of sustained efforts in this direction for the last almost six decades, one might on a superficial level, conclude that all major/important conceptual developments have already occurred, and it is only left to improve the accuracy—the "next decimal place" in the phraseology of some nineteenth century physicists. That this is not so is quite apparent, if one geocs through the literature on rotational analysis of the past few years. The sustained effort on the spectroscopy of H_2 and its isotopic species almost in step with improved theoretical description of this simplest of all molecules, has resulted in the hands of Herzberg in several new concepts—one very interesting result being the observation of Frank-Condon intensity fluctuations in the region close to the absorption limit. A more beautiful evidence on the correctness of the wave mechanical description of molecular structure would be hard to find. Very recently the existence of diatomic molecules containing two closed shell atoms has once again proven the inadequacies of simple descriptions of chemical valence (Dabrowski and Herzberg 1978, Coxon *et al* 1975).

The types of problems which need to be clarified by further studies are of different nature in different groups of molecules. Thus in the case of light molecules (belonging generally to the first half of the periodic table, oxides, halides as well as homonuclear diatomics of first, second and to some extent the third row of the periodic table) the problems under active investigation include spin orbit interaction, centrifugal stretching interactions and their variation with vibration and rotation in addition to the discovery of new species. In the case of heavier as well as weakly bound diatomics there are great problems due to overlapping of bands, closeness of the different rotational lines, and in case of molecules containing rare earth elements the multiplicity of the electronic states as well as their large number in close proximity of the ground state, which have prevented even such analyses which are routine for light molecules.

The development of lasers with emission at several fixed frequencies as well as tunable frequency dye lasers has given impetus to the use of photoluminescence

spectra for the determination of rotational constants. The basic advantage of the laser as source of excitation of photoluminescence is of course its intenxity and monochromaticity which permits the excitation of single rotational levels in the excited electronic states. The luminescence spectrum therefore consists of very few lines corresponding to each vibrational level of the lower state, which makes for easy and unambiguous J assignments. The advantages of laser photoluminescence over other emission spectra are :

i) One gets cleaner spectrum with large signal to noise ratio.

ii) Information can be accumulated efficiently from the measurement of a relatively small number of significant lines.

iii) The development of rotational structure from a simple R, P doublet on one hand to a band with lines of a broad range of J values on the other may be controlled at will by varying the pressure of the molecular vapour in the flouresconce cell. This also points to the possibility of studying collisional relaxation mechanisms.

These advantages can be utilised to the maximum effect only when a reasonably accurate idea of the ground state rotational constants is available and the type of electronic transition is known from independent data. Another source of some ambiguity is the presence of several isotopic species. In normal emission work the abundance ratio of different isotopes determines the intensity ratios of the isotopic lines but in laser excitation this is no longer true. For if the laser line happens to be coincident with a rational line of the less abundant isotope, only this isotope would give fluorescence spectrum.

The analysis of the fluorescence spectrum follows the following basic steps :

The line positions $\nu(v', J'; v'', J'')$ of a photoluminescence series may be represented (Herzberg 1950) as

$$\nu(v', J'; v'', J'') = \nu_e + G(v') - G(v'') + F_{v'}(J') - F_{v''}(J'') \quad (1)$$

where

$$G(v) = w_e(v+\tfrac{1}{2}) - w_e x_e(v+\tfrac{1}{2})^2 + w_e y_e(v+\tfrac{1}{2})^3 - w_e z_e(v+\tfrac{1}{2})^4 + \ldots \quad (2)$$

and

$$F_v(J) = B_v[J(J+1) - \Lambda^2] - D_v[J(J+1) - \Lambda^2]^2 + \ldots \quad (3)$$

with

$$B_v = B_e - \alpha_e(v+\tfrac{1}{2}) + \gamma_e(v+\tfrac{1}{2})^2 + \ldots \quad (4)$$

$$D_v = D_e + \beta_e(v+\tfrac{1}{2}) + \delta_e(v+\tfrac{1}{2})^2 + \ldots \quad (5)$$

The separation between pairs of lines $v', J'; v'', J''$ and $v', J'; v''+1, J''$ of the same photoluminescence series i.e. $\Delta\nu_{v''b}$ can be written as

$$\Delta\nu_{v''b}(v) = a_0 - a_1 v + a_2 v^2 + \ldots \quad (6)$$

with

$$a_0 = w_e - 2w_e x_e + 3{\cdot}25 w_e y_e + 5 w_e z_e + (-\alpha_e + 2\gamma_e) J(J+1) - (\beta_e + 2\delta_e)[J(J+1)]^2 \quad (7)$$

$$a_1 = 2w_e x_e - 6 w_e y_e - 13 w_e z_e - \gamma_e J(J+1) + 2\delta_e [J(J+1)]^2 \quad (8)$$

$$a_2 = 3 w_e y_e + 12 w_e z_e. \quad (9)$$

The constants a_0, a_1, a_2 etc. can be obtained by least squares fitting. Correlations between the various parameters some times lead to different values of the constants which reproduce the data with almost similar deviations.

Also, the spacing between the doublet lines v', J'; v'', $J'+1$ and v', J'; v'', $J'-1$ of a P and R photoluminescence series is given by

$$\Delta\nu_{rot}(v) = b_0 - b_1 v + b_2 v^2 \quad (10)$$

with

$$b_0 = (4B_e - 2\alpha_e + \gamma_e)(J' + \tfrac{1}{2}) \quad (11)$$

$$b_1 = (4\alpha_e - 4\gamma_e)(J' + \tfrac{1}{2}) \quad (12)$$

$$b_2 = 4\gamma_e (J' + \tfrac{1}{2}) \quad (13)$$

in which higher orders of J' and the small contributions of the D_v term is neglected. Again least squares procedures could be used to obtain the constants.

The J' and the lower state vibrational quantum number are fixed as follows. Using the known or estimated B_e'' value the separation of the PR doublet gives

$$J' + \frac{1}{2} = \frac{\Delta\nu_{rot}(PR)}{4B_v''} \cong \frac{\Delta\nu_{rot}}{4B_e''} \quad (14)$$

In most cases this fixes the J numbering uniquely, but in some cases this may be indefinite by upto one unit. The existence of anti-stokes doublets in the photoluminescence series indicates in general whether the v'' value of the excited rotational line is greater than zero. Further information about the vibrational assignments can be obtained using the vibrational intensity distribution and Franck-Condon factor data. A very detailed and exhaustive review is given in two papers on Bi_2 by Broaida and his coworkers (Gerber *et al* 1976).

3. Examples of the study of laser photoluminescence of diatomic molecules

Bi_2 (Gerber *et al* 1976)

Bismuch diatomic molecules produced in a heat pipe oven at various pressures are excited by using various Ar^+ laser lines. In addition to the known electronic states four new electronic states have been observed. In several electronic transitions the fluorescence series extends over both limbs of the Condon parabola. It is found that the hitherto known X-state is not the ground state but lies above the actual ground state by $\sim$1500 cm^{-1}. In excitation by the 5145 Å line a continuous emission from an unbounded upper state is also observed.

Te_2 (Stone and Barrow 1975) and Se_2 (Greenwood and Barrow 1976)

Even though Te_2 spectrum has been under investigation since 1957 a satisfactory rotational analysis was first performed in 1972 by Barrow and du Parcq who used enriched isotopes. The separation between $X1$ (a component of $^3\Sigma_g^-$) and $X0_g^+$ was estimated as 2820 ± 320 cm^{-1}. Laser fluorescence study at low and high resolution were then carried out and fluorescence series due to the transitions $B0_u^+$–$X1_g$ and $B1_u$–$X1_g$ were also observed. This led to a revision of the above value to a lower estimate of 1975 cm^{-1}. A similar situation existed in Se_2 where earlier estimates of the separation $X1_g$–$X0_g^+$ was 3679 cm^{-1}. The revised value of 509·95 cm^{-1} brings the predissociation observed in the $v = 5$ level of $B1_u$ ($J \sim 72$) state into agreement with the limiting curve of dissociation obtained from $v = 4, 5, 6$ of $B0_u^+$.

TiO (Linton and Broida 1977)

TiO is a molecule of astrophysical interest and has been extensively investigated spectroscopically (Linton and Singhal 1974, Hocking *et al* 1979). This data is however incomplete in several respects e.g. vibrational constants of most of the singlet states are not known with accuracy and the separation between the lowest singlet and the ground $^3\Delta$ state was not in agreement with theoretical estimates. The $a^1\Delta$–$X^3\Delta$ separation was estimated as 581 cm^{-1} by the study of temperature variation of singlet and triplet band intensities. SCF-MO calculations lead to a value of 4430 cm^{-1} which may not be in error by more than a factor of 2. A study (Brom and Broida 1975) of laser photoluminescence of TiO trapped in Ne matrix at 4°K led to the observation of $b^1\pi$–$X^3\Delta$ transition which could with the earlier observed $b^1\pi$–$a^1\Delta$ transition lead to a value of $\sim$3500 cm^{-1} for $a^1\Delta$–$X^3\Delta$ separation. A very interesting case of intersystem transfer of excitation from $B^3\pi(v = 0$ and $v = 1)$ to $b^1\pi$ ($\pi = 1$ and $v = 0$) was also observed. In later work (Linton and Broida 1977) the separation $a^1\Delta$–$X^3\Delta$ has been redetermined in the gas phase as 3444 ± 10 cm^{-1}. A new $C^3\Delta$–$a^1\pi$ transition was also observed. Collisional transfer of excited molecules from $C^3\Delta$ ($v = 2$) to $c^1\Phi$ state was also detected.

CuI

The emission spectrum of the A–X system of the CuI molecules excited in an electrical discharge through the molecular vapour and recorded (Mishra *et al* 1979) on our grating spectrograph is shown in Figure 1 where the rotational assignments are also shown. The analysis shows the transition to be $A^1\pi$–$X^1\Sigma^+$. The fluorescence spectrum excited by the 5145 Å line of the Ar^+ laser (Wu and Dows 1975) is shown in Figure 2. The difference between the multimode and single mode excitation is seen from Figure 3 where in the region 19150–19200 cm^{-1} of the fluorescence is shown in detail. As seen in the figure single mode excitation at the point A of the gain profile (see Fig. 4) gives rise to a doublet with

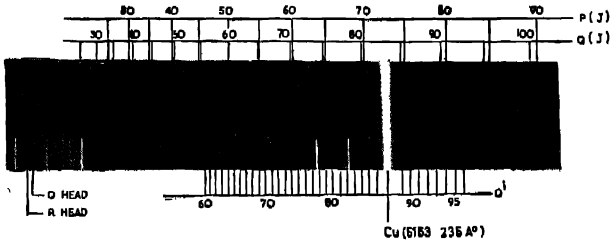

Figure 1. Rotational structure in the (0,1) band of the A-X system of CuI molecule

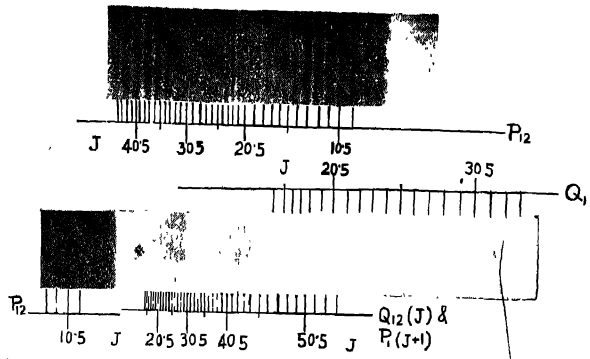

Figure 6. Rotational Structure in the (0,0) band of the $A^2\pi - X^2\Sigma^+$ System of CaF

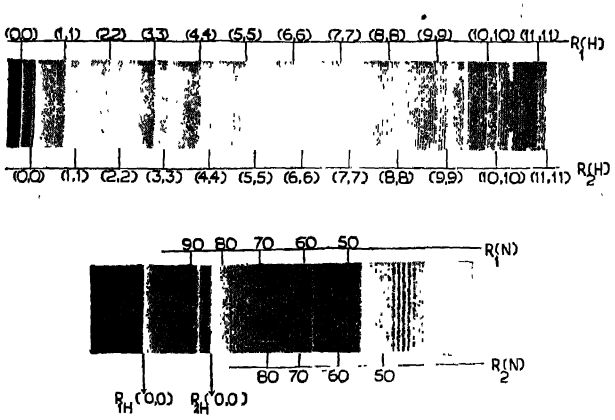

Figure 7. Vibrational structure in (0,0) sequence and rotational structure in (0,0) band of the $B^2\Sigma - X^2\Sigma$ system of CaF molecule

a doublet splitting of $\sim 13{\cdot}1\ cm^{-1}$, excitation by the laser in the mode B gives rise to a doublet with a doublet splitting of $\sim 20{\cdot}8\ cm^{-1}$, while excitation by mode C gives rise to a singlet. In the multimode excitation all the five lines are present.

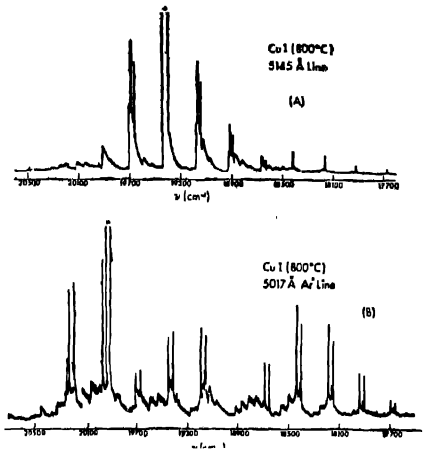

Figure 2. Resonance Fluorescence Spectra obtained by the Excitation of CuI at temperature of 800°C with(a) 5145 and (b) 5017 A laser lines

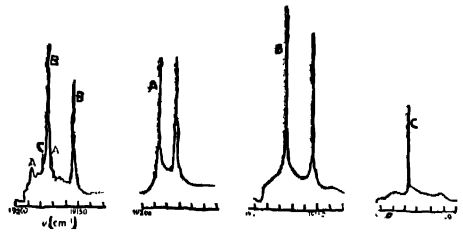

Figure 3. Fluorescence in the first Stokes bands of CuI Excited by Multimode 5145Å Radiation. The Doublets A-A and B-B, and the Singlet C, are obtained when single mode excitation at the corresponding points A,B, and C in Fig. is used

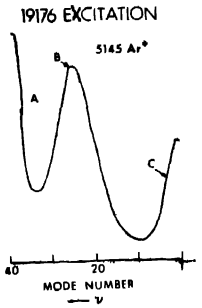

Figure 4. Excitation Spectrum of 19176 cm^{-1} fluorescence of CuI as a function of longitudinal mode of laser operation in the 5145 Å line. Mode separation is ~143 MHz. The intensity has been corrected for laser power

An energy level diagram showing the possible rotational transitions in a $^1\pi \rightarrow {}^1\Sigma^+$ transition is shown in Figure 5. Each rotational level in the $^1\pi$ state split into two Λ-components e and f with opposite parity. It is seen that P and R branch lines involve one component while the Q branch lines arise from transitions originating in the other Λ-component. The splitting constant for the upper state is 2×10^{-5} cm^{-1} hence except at very low values of J the single mode laser line will excite only one of the two components. Depending upon

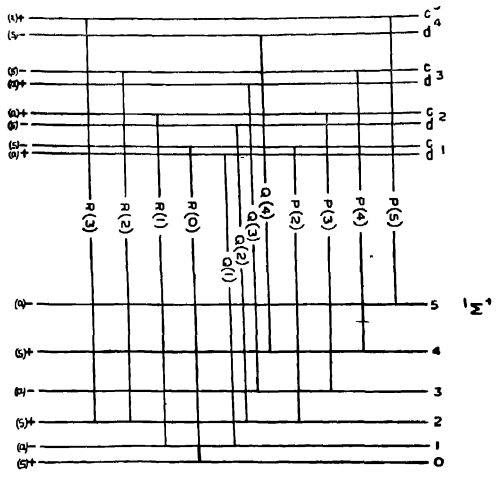

Figure 5. Energy Level Diagram for a $^1\pi$—$^1\Sigma^+$ Transition

the Λ-component of the upper state which gets excited the fluorescence would either consist of doublets due to P and R branch lines or singlets due to Q branch. The J numbering of the P and R branch lines would be $(J'+1)$ and $(J'-1)$, while for the Q branch it would be J'. This indicates that in the fluorescence spectrum the singlet is a Q branch line while the doublets are pairs of P and R branch lines. The separation $R(J-1)-P(J+1)$ is given by the relation

$$R(J-1)-P(J+1) = \Delta_2 F''(J)$$
$$= 4B_v''(J+1)-8D_v''(J+\tfrac{1}{2})^3$$

and hence the observed doublet splittings can be used to determine J since B_v'' and D_v'' are known. This fixes the J for the A doublet as 44 and for the B doublet as 72.

Wu and Dows (1975) have explained the five lines in the region 19150–19200 cm^{-1} as the $P(45)$ and $R(43)$ lines of (0, 1); $R(71)$ and $P(73)$ lines of (0, 1) and the C singlet line as being due to overlapping of two lines. This is clearly incorrect. Their table (1) shows that the laser line at 5145 Å coincides in the A-mode with $P(45)$, and in the B mode with lines of the R and P branches with $J' = 71$, of the (0, 1) band. The measured wavenumbers of the rotational lines in the (0, 1) band indicate that $P(45)$ of this band does have the same wavenumber has the laser line but neither $P(72)$, $R(71)$ nor $Q(71)$ of ^{65}CuI (also of ^{63}CuI) is coincident in energy with the laser line in mode B. Mode C wavelength is coincident with $Q(44)$ of ^{63}CuI (0, 1) band.

Table 1. Observed resonance fluorescence lines induced by various argon ion laser lines

5145Å A-Single Mode (a)		B-Single Mode		C-Single Mode	
(v',v'')	cm^{-1}	(v',v'')		(v',v'')	
0,0	19702	0,0	19692.7	0,0	19704.5
	19688		19671.9		
	19442				
0,1	laser line	0,1	laser line	0,1	laser line
0,2	19183	0,2	19173.6	0,2	19178.1
	19170		19152.7		
0,3	18926		18914.7	0,3	18917.0
	18913		18894.1		18917.0
0,4	18669	0,4	18659.3	0,4	18657.0
	18656		18639.0		
		0,5	18884·4	0,5	18398.8

In their work Wu and Dows (1975) have observed excitations from vibrational levels for which v'' is as large as 6 so we felt it desirable to search coincidences

between the wavenumber of the B-mode of the laser and some rotational transition of bands involving v'' values larger than 1. A preliminary search using vibrational constants of the two states showed that another band whose rotational lines may be expected to coincide with the laser line is the (4, 4) band. More careful comparisons showed that the $P(72)$ line of this band of ^{63}CuI is coincident with the laser line. It is therefore obvious that fluorescence doublets arising due to the B mode would have wavenumber separations corresponding to $\Delta_2F''(71)$ of the $v = 4$ level of the ground state. Use of the known B_e, α_e and D_e values does confirm this point. Further, making use of the relations (6), (7) etc. one can obtain $\Delta G''_{v+\frac{1}{2}}$ values for the different v values of the lower state. An analysis along these lines with the vibrational assignments given by Wu and Dows (1975) yields $w''_e \sim 259$ cm^{-1} for ^{65}CuI whereas from analysis of other systems involving the same X state, this value is known to be ~ 263 cm^{-1}. Increasing the vibrational numbering in the two states so that (0, 1) band is relabelled as (4, 4) brings the two values into coincidence. Thus, we assumed that the vibrational assignments given by Wu and Dows (1975) of the fluorescence doublets arising due to the B-mode excitation are incorrect and need to be changed by increasing v' by 4 units and v'' by 3 units.

These modified assignments and modifications permit us to determine the rotational and vibrational constants of the various vibrational levels of the $X^1\Sigma$ state.

CaF

Two band systems are known for the CaF molecule in the visible region. These are ascribed to the $A^2\pi$–$X^2\Sigma^+$ and $B^2\Sigma^+$–$X^2\Sigma^+$ transitions. The band systems are characterized by very close sequence bands and earlier attempts to resolve the rotational structure in optical emission or absorption had proved futile. A partial analysis was performed by Mohanty (Mohanty and Upadhya 1967) (Figure 6) in our laboratory and a much more accurate study was performed by Field *et al* (1975) on the A–X system. Very recently microwave optical double resonance technique (Nakagawa *et al* 1978) has been utilised to further improve the rotational constants of the $A^2\pi$ and the $X^2\Sigma^+$ states (Nakagawa *et al* 1978).

The B–X system has been photographed in emission in our laboratory again and the (0, 0) and (1, 0) bands have been analysed rotationally (Ram *et al* 1979). The molecular constants for the Zeroeth vibrational level of the X state have been taken from the last mentioned work. The spectrum is shown in Figure 7 and it is seen that one is able to utilize only a very small fraction of the available data.

Fortunately, the 5145 Å line of the Ar^+ laser coincides in wavelength with the head of the (1, 0) band so that its use is expected to lead to significant advantage in simplifying the observed emission spectrum.

Acknowledgments

The author is thankful to Dr. S B. Rai for several discussions on the spectrum of CuI and for other help in the preparation of the paper. He is also thankful to Professor Dows for permitting him to use the figures and tabular material from his published paper (ref 12)

References

Dabrowoski J and Herzberg G 1978 *J. Mol. Spectrosc.* **73** 183
Coxon J A Jones W E and Subbaram K V 1975 *Can. J, Phys*, **53** 2016 2321
Herzberg G 1950 *Spectra of Diatomic Uolecvles*, Van Nostrand, N Y
Gerber G Sakural K and Brlida H P 1976 *J. Chem. Phys.* **64** 3410
Stone T J and Barrow R P 1973 *Can. J. Phys.* **53** 1976
Greenwood D J and Barrow R F 1976 *J. Phys. B(Atom. & Moles. Phys.* **9** 2123
Linton C and Broida H P 1977 *J. Mol. Spectrosc.* **64** 389
Linton C and Singnal S R 1074 *J. Mol. Spectrosc.* **51** 194
Hocking W R Gerry M C L and Merrer A J 1979 *Can. J. Phys.* **57** 54
Brom J H Jr and Broida H P 1975 *J. Chem. Phys.* **63** 3718
Mishra G P Rai S B and Upadhya K N *Can. J. Phys.* **57**
Wu C R and Dows D A 1975 *J. Mol. Spectrosc.* **58** 384
Mohanty B S and Upadhya K N 1967 *Ind. J. Pure & Appl. Phys.* **5**, 523
Field R W Harris D O and Tanaka T 1975 *J. Mol. Spectry.* **57** 107
Nakagawa J Domaille P J Steimle T O and Harris D O 1978 *J. Mol. Spectrosc.* **70** 374
Ram R S Rai S B and Upadhya K N 1979 *Pramana* **13**, 149